

UNCLASSIFIED



AD NUMBER

AD-835 120

CLASSIFICATION CHANGES

TO UNCLASSIFIED

FROM NEVER CLASSIFIED

AUTHORITY

Aerospace Technology Div, Library of Congress,  
Washington, DC; Jun 29, 1968

19990805016

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED



AD NUMBER

AD-835 120

NEW LIMITATION CHANGE

TO

DISTRIBUTION STATEMENT: A

Approved for public release; Distribution unlimited.

LIMITATION CODE: 1

FROM

No Prior DoD Distr Scty Cntrl St'mt Assgn'd

AUTHORITY

Aerospace Technology Div, USAF Ltr; Nov 27, 1968

THIS PAGE IS UNCLASSIFIED

ATD Report 68-72-106-3

29 June 1968

*Surveys of Foreign Scientific and Technical Literature*

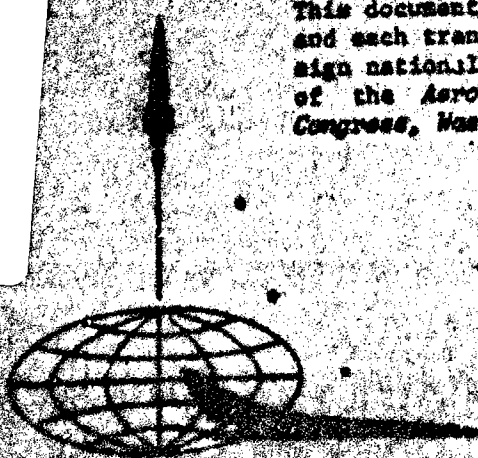
AD835120

# THE FOREIGN TECHNOLOGY OF SOLID PROPELLANTS AND THEIR COMBUSTION

Serge Markov

Reproduced From  
Best Available Copy

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Aerospace Technology Division, Library of Congress, Washington, D. C. 20540.



Aerospace Technology Division  
Library of Congress



ATD Report 68-72-106-3

29 June 1968

*Surveys of Foreign Scientific and Technical Literature*

THE FOREIGN TECHNOLOGY OF SOLID PROPELLANTS AND  
THEIR COMBUSTION

ATD Work Assignment No. 106  
(Report No. 3 in this series)

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the *Aerospace Technology Division, Library of Congress, Washington, D. C. 20540.*

The publication of this report does not constitute approval by any U. S. Government organization of the inferences, findings, and conclusions contained herein. It is published solely for the exchange and stimulation of ideas.

Aerospace Technology Division  
Library of Congress

## FOREWORD

This is Report No. 3 of a series which provides coverage of current Communist-world open literature available at the Library of Congress on the technology of solid propellants and their combustion, in the form of periodic analytical studies. This report is based on materials which, for the most part, became available during the period December 1967--March 1968. The literature selected is reviewed and the rationale behind the selection of individual items is discussed in terms of subject, author, authors' previous work, and when determinable, authors' affiliations. The items reviewed are full-size papers unless otherwise specified. Comments by the ATD analyst are italicized. There are 22 references arranged in the order in which they appear in the report.

UNCLASSIFIED

## TABLE OF CONTENTS

### FOREWORD

TECHNOLOGY OF SOLID PROPELLANTS . . . . .	1
Preparation and production of propellant ingredients . . . . .	1
Properties of propellant ingredients . . . . .	2
COMBUSTION OF SOLID PROPELLANTS . . . . .	5
Combustion of solid propellants . . . . .	5
Thermal decomposition of solid propellants . . . . .	11
Ignition . . . . .	14
Thermal explosion . . . . .	15
Detonation . . . . .	19
REFERENCES . . . . .	23

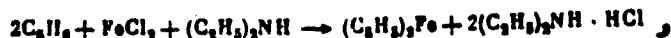
## TECHNOLOGY OF SOLID PROPELLANTS

Preparation and production of propellant ingredients. A short (16-line) article [1] concerns the synthesis of 1,1,1,6,6,6-hexanitrohexane which may be of interest as a plasticizer for solid propellants. 1,1,1,6,6,6-Hexanitrohexane (mp, 164°C) is formed in 40% yield along with 1-fluoro-3,3,3-trinitropropane on treatment of a suspension of 1,1,1-trinitro-3-bromomercuropropane or bis(3,3,3-trinitropropyl)mercury with free fluorine diluted with nitrogen (1/5) in carbon tetrachloride at 40—50°C. 1,1,1,6,6,6-Hexanitrohexane remains in the residue after volatile products have been stripped off from the reaction mixture. The authors of this item are with the Institute of Chemical Physics, AS USSR.

An Author Certificate [2] has been issued for a propellant for model rockets, whose principal ingredients are potassium perchlorate, a synthetic resin, and magnesium powder. To increase the energetic characteristics of the propellant, the proportions of the ingredients are as follows:

potassium perchlorate	81 ± 2.0%
furfural-cyclopentadiene resin	17.7 ± 1.0%
magnesium powder	1.3 ± 0.2%
acetone	up to 1.0% (over and above 100%)

An article [3] reports the production of ferrocene on a pilot plant scale. It may be of interest as an indication of a Soviet effort to upscale the production of ferrocene, possibly to quantities commensurate with the use of ferrocene as an additive to propellants. The process uses a unit (diagrammed in the original) that is simple in design and may serve as a model for up-scaling the production of ferrocene to a semi-plant level. The process is based on the so-called "amine" preparative method for ferrocene,



which, however, has been considerably simplified and from which a number of organic solvents undesirable in production have been eliminated. The ferrocene obtained is of adequate purity and the yield is good (90—95% on  $FeCl_2$ ). The capacity of the unit is 2 kg ferrocene per batch. The process involves the following steps: 1) depolymerization of the cyclopentadiene dimer; 2) dehydration of the ferrous chloride hydrate; 3) synthesis of the ferrocene; 4) distillation of the ferrocene; 5) water wash and drying of the ferrocene. The water wash ensures the requisite purity of the product.

Properties of propellant ingredients. Two items in this section may be of interest from the standpoint of double base propellants. The first paper [4] is Communication V of a series by D. V. Balashov (who is associated with the Institute of Heteroorganic Compounds, AS USSR) dealing with the thermodynamic properties of nitroglycerin explosives at pressures of up to 26000 kg/cm<sup>2</sup> in the 20—92°C range. (Communications I—III were covered in ATD Report 67-32, Ref. 3—5, 3—6, and 3—7, and Communication IV in ATD Report 68-30-106-2, Ref. 9). This particular paper reports the results of an experimental study of the pressure dependence of the temperature and density of the ballistite-type nitroglycerin powders N, NB-40, and NB-60 containing 28, 40, and 60% nitroglycerin, respectively, in the isentropic compression to 26000 kg/cm<sup>2</sup>. The temperature, adiabatic temperature effect of compression  $(\partial T/\partial p)_s$ , and the density of the powders were plotted (see Fig. 1, 2, and 3) and tabulated as a function of pressure at different constant entropies. It was found that temperature rises with pressure up to a peak at 4400—193000 kg/cm<sup>2</sup>, where for the various powders  $(\partial v/\partial T)_p = 0$ ; at higher pressures when  $(\partial v/\partial T)_p < 0$ , temperature drops.  $(\partial T/\partial p)_s$  decreases with increasing pressure; at 4400—10300 kg/cm<sup>2</sup>,  $(\partial T/\partial p)_s$  isotherms go through zero and on to negative values. On going to isotherms corresponding to higher entropies, the rate of heating of the powders in the process of

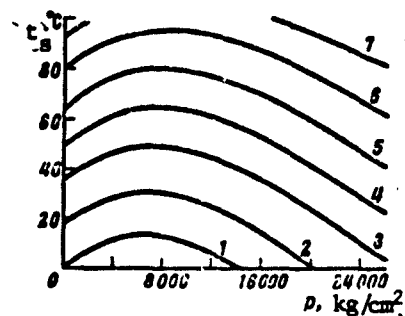


Fig. 1. Adiabatic temperature effect of compression  $(T/p)_s$  of nitroglycerin powder NB-40 versus pressure  $(p)$  in isentropic compression:

- 1 - Specific entropy  $s = 0.024$ ;
- 2 -  $s = 0.089$ ; 3 -  $s = 0.129$  cal/g·°C.

compression at  $(\partial v/\partial T)_p > 0$  first increases and then decreases while the rate of cooling at  $(\partial v/\partial T)_p < 0$  decreases. The thermodynamic properties considered above are dependent on the nitroglycerin content of the powders; this is evidently due to a change in the interaction of the phases in the nitroglycerin-pyroxilin system at high pressures and temperatures. In the case of density, its value at 26000 kg/cm<sup>2</sup> was 0.5—2.5% less than in isothermal compression. The calculated isentropic densities of N powder were in satisfactory agreement with densities previously obtained in shock compression; the deviations of



about 2% can be explained by a difference in the thermal effects in isoentropic and shock compression. An approximate calculation of the

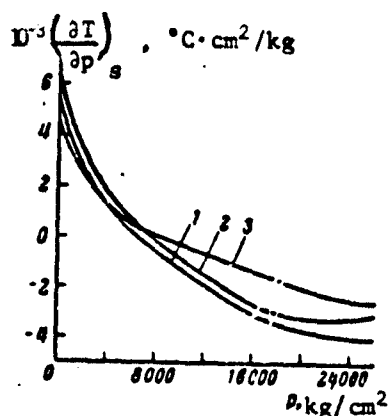


Fig. 2. Density ( $\rho$ ) of nitroglycerin powder N versus pressure ( $p$ ,  $\text{kg}/\text{cm}^2$ ) in isoentropic compression:

1 - Specific entropy  $s = 0.022$ ;  
2 -  $s = 0.084$ ; 3 -  $s = 0.121$   
 $\text{cal}/\text{g}^\circ\text{C}$ ; 4 - previously obtained  
data for shock compression.

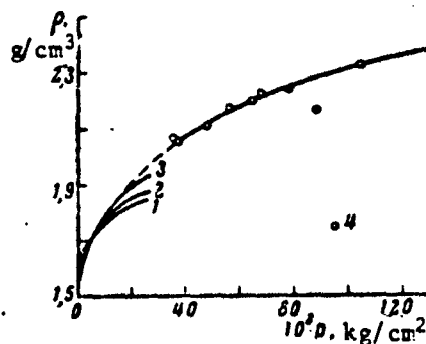


Fig. 3. Temperature ( $t_g$ ) of nitroglycerin powder NB-40 versus pressure ( $p$ ) in isoentropic compression:

1 - Specific entropy  $s = 0$ ;  
2 -  $s = 0.024$ ; 3 -  $s = 0.050$ ;  
4 -  $s = 0.070$ ; 5 -  $s = 0.089$ ;  
6 -  $s = 0.110$ ; 7 -  $s =$   
 $0.129 \text{ cal}/\text{g}^\circ\text{C}$ .

temperature corresponding to the shock adiabat was made. The temperature rises from  $20^\circ\text{C}$  at atmospheric pressure to  $95^\circ\text{C}$  at  $10,000 \text{ kg}/\text{cm}^2$  and then decreases smoothly to  $70^\circ\text{C}$  at  $26,000 \text{ kg}/\text{cm}^2$ . Professor A. I. Kitaygorodskiy is credited with giving guidance to the author of this item.

The equation of state of crystalline trinitrotoluene is derived by the Debye-Einstein-Gruneisen method in an article [5] whose authors are connected with the Institute of Physics of the Earth im. O. Yu. Schmidt, AS USSR.

An article [6] appears to be of interest as a signal indicating the existence of ongoing research on the effect of the crystalline structure of the binder in ammonium perchlorate-epoxy resin composite propellant systems on the chemical, physical, and mechanical properties of the systems. The article reports that an x-ray analysis and electron microscope study have been made of boundary layers formed by

molecules of ED-5 epoxy resin on the surface of ammonium perchlorate crystals. Epoxy monomer was applied to the ammonium perchlorate crystals from a solution in acetone; this was followed by curing with maleic anhydride. It was found that under certain conditions, the polar molecules of ED-5 monomer can form metastable vertically or horizontally oriented structures on the surface of  $\text{NH}_4\text{ClO}_4$  crystals. Polymerization of the monomer under these conditions results in a boundary layer with a stable, crystalline structure. The crystalline boundary layer of ED-5 molecules can have a substantial effect [unspecified] on the chemical, physical, and mechanical properties of the ammonium perchlorate crystals proper and of the ammonium perchlorate-ED-5 system as a whole. It is noted that by virtue of oriented adsorption, a boundary layer of polar molecules on a solid exhibits good mechanical properties in the direction perpendicular to the solid's surface. The ED-5 film increases the resistance of the ammonium perchlorate to fast electrons which otherwise cause rapid decomposition. The authors of this item are with Leningrad Technological Institute in Leningrad.

A paper [7] by workers associated with Tomsk Polytechnic Institute and Moscow State University deals with the radiolysis of ammonium perchlorate and *may therefore be of interest from the standpoint of the effect of ionizing radiation on this oxidizer*. This study was done because, in contrast to alkali and alkaline earth perchlorates, there is a paucity of data on the radiolysis of ammonium perchlorate in which a different decomposition mechanism of the perchlorate ion could be expected as a result of reducing-agent formation in the radiolysis of the ammonium ion. This particular communication deals with results of the investigation of conversion products of the  $\text{ClO}_4^-$  ion in  $\text{NH}_4\text{ClO}_4$  under the action of 4.7 Mev protons. A  $30 \text{ mg/cm}^2$  layer of  $\text{NH}_4\text{ClO}_4$  powder was irradiated by a method described earlier at an average dose rate of  $1.8 \times 10^{20} \text{ ev/g min}$ . The sample was analyzed and the results are presented in the form of plots of the concentration of  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ ,  $\text{Cl}_2$ , and  $\text{Cl}^-$  formed versus dose. At small doses up to  $1.6 \times 10^{21} \text{ ev/g}$ , all the plots are linear; at higher doses the  $\text{ClO}_3^-$  concentration reaches a plateau while the  $\text{Cl}^-$  concentration increases more steeply. This is attributed to the thermal decomposition of ammonium chlorate which is unstable at room temperature. Comparison of radiation yields under proton irradiation with previously obtained  $\gamma$ -ray radiation yields indicates that the yields are nearly the same for the different species involved with the exception of  $\text{Cl}^-$  ions whose yield under the action of protons is  $\sim 1/1.5$  that in  $\gamma$ -radiolysis. The results of this study confirm the absence of local hot spots in heavy-particle tracks.

## COMBUSTION OF SOLID PROPELLANTS

Combustion of solid propellants. N. N. Bakhman and the late A. F. Belyayev of the Institute of Chemical Physics, AS USSR, who are prominent authorities in the area of solid propellant combustion (they are the authors of a recent review article [ATD Report 67-33, Ref. 4-2] on the current state of development of the combustion theory of explosive and solid rocket propellants, and of a monograph [ATD Report 68-29-106-1, Ref. 5] on the combustion of heterogeneous condensed systems) have written a critical review [8] of K. K. Andreyev's monograph *Thermal Decomposition and Combustion of Explosives* (Second edition revised and expanded), Moscow, 1966 which deals with the thermal decomposition, stable and unstable combustion, ignition, and explosion of explosives. The author is himself a recognized authority in the area of theory of explosives. This review may be of interest from the standpoint of certain comments made by the authors. Among the shortcomings associated with the book, Bakhman and Belyayev list the following: 1) the small size of the edition (2700 copies printed); 2) the inadequate treatment of the combustion of heterogeneous systems; 3) the fact that the research of A. G. Merzhanov, G. B. Manelis, F. I. Dubovitskiy, et al., of the Institute of Chemical Physics, AS USSR, on the thermal decomposition and thermal autoignition (thermal explosion) of explosives is not treated although it has very substantially developed both investigative methods and fundamental ideas; 4) the fact that the true significance of the Zel'dovich theory, which is that it establishes a simple and reliable relationship between the burning velocity and the chemical reaction rate in the combustion zone, is not made clear. These comments of Bakhman and Belyayev provide a hint concerning the size of the community of potential users of such a book and concerning areas of research which are of significance from the viewpoint of these authorities. (The reviewers stress, however, that these and other defects of the monograph do not significantly detract from the value of the book which, they say, should become a standard reference text for scientists dealing with the combustion of explosives and allied condensed systems, combustion stability, and deflagration-detonation transition; the book is also invaluable for workers of explosive manufacturing plants, and for senior students of the appropriate disciplines).

A theoretical article [9] may be of interest as it gives an analysis of the combustion stability of solid propellants and derives certain criteria of stable combustion. It is noted that the temperature gradient ( $\phi$ ) on the surface of the foam zone plays an important part in the study of the combustion of powders. In steady-state regimes,

$\phi$  is determined by the expression,

$$\phi = u\lambda^{-1} (T_1 - T_0), \quad (1)$$

where  $u$  is the burning velocity,  $\lambda$  is the thermal diffusivity,  $T_1$  is the surface temperature of the powder, and  $T_0$  is the temperature of the cold powder. The behavior of  $\phi$  with  $T_0$  is of great significance. Ya. B. Zeldovich's postulate that  $\phi = f(T_0)$  has a maximum where  $d\phi/dT_0 = 0$ , so that combustion is stable if  $d\phi/dT_0 < 0$ , and unstable if  $d\phi/dT_0 > 0$ , was reported in the literature not to be valid in all cases. A verification of the fundamental postulate of the existence of a maximum  $\phi$  was therefore of interest. To make such a verification possible, the right-hand side of the above equation should contain only one variable,  $u$  or  $T_0$ . An expression relating  $u$  to  $T_0$  was therefore derived and substituted into (1) to give,

$$\phi = \frac{(T_1 - T_0)u}{\lambda_1} = \frac{1}{k_1} \left[ \frac{k_2}{\lambda_2} \sqrt{2J} \exp \frac{\alpha u l}{\lambda_2} - q\rho_1 u \right], \quad (2)$$

where  $k$  is thermal conductivity;  $\alpha = \rho_1/\rho_2$ ;  $l$  is the distance of flame propagation;  $\rho$  is density;  $J = \int_{T_1}^{T_2} F(T)dT$ ,  $J$  is obtained with adequate approximation by graphical integration;  $q$  is the heat released or absorbed in the foam zone; and subscripts 1 and 2 refer to the foam zone and the gas, respectively. Analysis of (2) shows that when  $q \geq 0$ ,  $\phi$  has no extremum but a limiting value (when  $T_0 \rightarrow \infty$ ) of  $k_2 k_1^{-1} \sqrt{2J/\lambda_2}$ ; when  $q < 0$ ,  $\phi$  has a minimum where  $d\phi/du = 0$ . These results confirm the existence of a limiting value of  $\phi$  for steady-state regimes. Steady state combustion is always stable if  $q > 0$ . If  $q < 0$ , combustion is stable when  $d\phi/dT_0 < 0$ , and unstable when  $d\phi/dT_0 > 0$ ; in the latter case, instability is not associated with extinguishment but acceleration of combustion. The author, S. A. Kaganov, gives credit to S. V. Fal'kovich for advisory comments on this article.

An article [10] recommended for publication by Academician N. M. Emanuel', a top Soviet physical chemist, appears to be of interest from the standpoint of the effect of additives on the combustion of ammonium nitrate and ammonium perchlorate composite propellants. This article deals with the effect on the burning rate of these perchlorates, of combustion inhibitors of the ammonium salt type, viz., ammonium carbonate, oxalate, citrate, tartrate, or fluoride, and of a reducing agent-type inhibitor, diphenylamine. It is noted that in the case of composite propellants, the need for inhibitors which will lower the burning rate is dictated by the demand for propellant compositions exhibiting a low pressure-dependence of the burning rate. Whereas, heretofore, the search for inhibitors as well as for catalysts

of combustion was, according to the authors, strictly empirical in character, in this research the problem was approached from the following theoretical considerations. It was postulated that readily dissociating ammonium salts would have the effect of shifting the equilibrium of the initial dissociation of ammonium nitrate and perchlorate (to ammonia and nitric acid, and ammonia and perchloric acid, respectively) to the left, while diphenylamine would either reduce or bind the acid formed, thereby inhibiting further oxidation of the ammonia. The effect of the additives (1—10%) was studied in a constant pressure bomb at pressures up to 1000 atm on the examples of amatol 80/20 (neat ammonium nitrate will not burn in a constant pressure bomb) and of ammonium perchlorate neat or in a stoichiometric mixture with coke. It was found that of all the inhibitors tested, ammonium carbonate has the strongest inhibiting effect for amatol, and ammonium fluoride, for ammonium perchlorate. On addition of ammonium carbonate to amatol, combustion terminated at 350 atm, while at 500 atm, the burning rate dropped to one half that for neat amatol. For the other additives including diphenylamine, the burning rate of amatol dropped on the average by a factor of 1.3—1.6 at 400 atm and of 1.5 at 950 atm. The character of combustion of amatol in the presence of the inhibitors changed with pressure; at up to 500 atm (for ammonium oxalate and carbonate) or at up to 750 atm (for ammonium tartrate or citrate) the flame showed horizontal stripes of greater or lesser brightness, which was attributed to the settling on walls of unburned particles, presumably carbon; at higher pressures the flame became more uniform. In the presence of ammonium fluoride, ammonium perchlorate burned in a stable manner only at 300 atm and above; at 200—250 atm combustion terminated; at up to 500 atm the burning rate dropped by a factor of 2.2 and at higher pressure, by 3.2. Addition of lithium fluoride to ammonium perchlorate decreased the burning rate by a factor of 5.7 at 100 atm, a factor of 3 at 150 atm, and of 2.8 at 900 atm. In the case of ammonium oxalate, ammonium perchlorate did not ignite at 100 atm and at 150 atm burned at a rate 1/3 that of neat ammonium perchlorate; the burning rate rose slowly with pressure up to 500—600 atm and faster at up to 1000 atm. Diphenylamine did not affect the capacity for combustion of ammonium perchlorate (it ignited at about 30 atm), but the burning rate of 150 atm dropped by a factor of 2.2 as compared with neat ammonium perchlorate; at 200—400 atm the burning rate was the same with or without diphenylamine, but at above 400 atm, ammonium perchlorate with diphenylamine burned again at a rate lower (by a factor of about 1.5) than neat ammonium perchlorate. Study of the effect of the presence of 10% of the additives ammonium oxalate, potassium oxalate, sodium chloride, potassium chloride, and ammonium chloride on the combustion temperature of amatol revealed that they all lower this temperature.

However, this effect was not the decisive one since ammonium oxalate decreased, while the other additives, increased the burning rate. This indicates that the chemical nature of the additive is the decisive factor; this was regarded as confirming the validity of the above postulate. The fact that the inhibiting effect of the additives, particularly in the case of amatol, was observed in the entire range of pressures studied may indicate that the dissociation reaction is rate-controlling.

The mechanism of action differs depending on the type of additive involved. In the case of the readily decomposing ammonium salts, their effect is similar on ammonium perchlorate and ammonium nitrate combustion, since ammonia is among the initial decomposition products in both cases. The picture is different on addition of the reducing agent-type inhibitor. In the case of ammonium nitrate, diphenylamine can react directly with one of the initial decomposition products, nitric acid. In the case of ammonium perchlorate, diphenylamine has a stronger effect at above 500 atm; this is evidently due to a different mechanism of ammonium perchlorate decomposition in this region, for example,



The authors of this item are with the Institute of Chemical Physics, AS USSR.

An article [11] co-authored by V. V. Boldyrev who is connected [15] with the Institute of Chemical Kinetics and Combustion, Siberian Branch, AS USSR and the Scientific Research Institute of Nuclear Physics at Tomsk Polytechnic Institute, and has recently been involved in studies concerned with the thermal decomposition of ammonium perchlorate [ATD Reports 67-26, Ref. 2-15; 67-33, Ref. 4-4; 68-29-108-1, Ref. 7] reports the first experimental results of research on the relationship between the burning velocity of an ammonium perchlorate composite propellant and the chemical structure of the fuel. Composite propellant samples containing 80% ammonium perchlorate with a particle size  $< 90 \mu$  and 20% fuel, pressed into grains  $8 \times 4 \times 35 \text{ mm}$  at  $1000 \text{ kg/cm}^2$  were used. The fuels tested were: 1) paraffin, 2) stearic acid, 3) palmitic acid, 4) azelaic acid, 5) citric acid, 6) pyrocatechol, 7) resorcinol, 8) hydroquinone, 9) biphenyl, 10) terphenyl, 11) quaterphenyl, 12) phenanthrene, 13) anthracene, 14) benzidine, 15) o-tolidine, 16) diaminodiphenylmethane, 17) tryptaflavine, 18) neutral

red, and 19) methylene blue. Burning velocity was measured at pressures of 1, 20, and 40 kg/cm<sup>2</sup> in a constant pressure bomb. Experimental results are plotted in Fig. 4. It was found that burning velocity depends

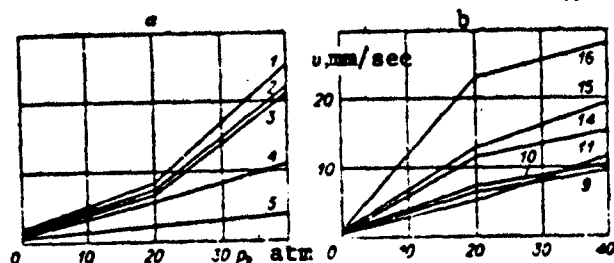


Fig. 4. Burning velocity of ammonium perchlorate-organic fuel mixtures versus pressure. (Numbers refer to compounds numbered in the text)

on the calorific value of fuels close in structure, and at a given calorific value, on chemical bond strength and molecular structure.

An article [12] may be of interest from the standpoint of the termination of combustion of propellants, which is of importance for missions requiring intermittent propulsion. This item reports the results of an experimental study of combustion termination by a rapid pressure drop for a nitroglycerin powder containing 2% MgO. The specimen grains were cylindrical, 8 mm in diameter and 10–13 mm high. The experimental procedure consisted in ignition of the specimen in nitrogen at a predetermined initial pressure (30–60 kg/cm<sup>2</sup>) followed by a release of a vent cover to produce a pressure drop. The apparatus was so designed that the absolute pressure drop and the rate of drop could be varied independently so as to determine which pressure drops cause termination of combustion. Experimental results are given in Figures 5–10. In Figures 5–10,  $H$  is the reduced final pressure,  $p_k$  is the final pressure;  $p_H$  is the initial pressure;  $W^*$  is the dimensionless rate of pressure drop;  $\dot{p}$  is the initial rate of pressure drop;  $\tau$  is the characteristic time of pressure drop, that is, the time it takes for the difference ( $\Delta p$ ) between the initial and final pressure to decrease by a factor of  $e$ ; the critical

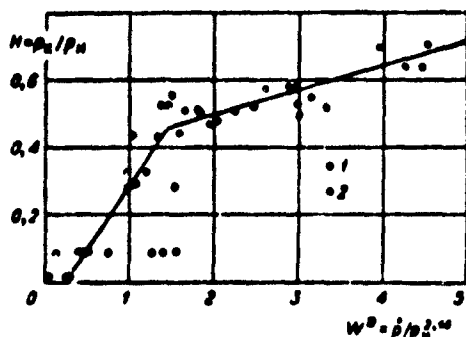


Fig. 5. Combustion termination curve for pressure drops from an initial level of 60 kg/cm<sup>2</sup>

1 - Pressure drops at which combustion terminated; 2 - pressure drops at which combustion proceeded to completion.

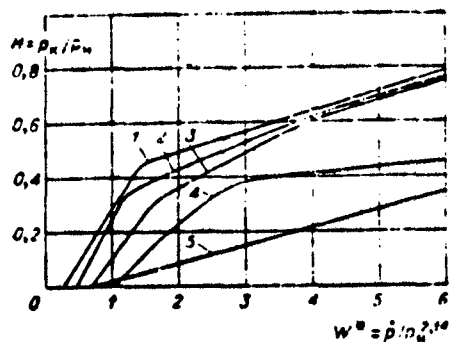


Fig. 6. Critical parameters of pressure drops

1,2,3 - Termination curves for pressure drops from initial levels of 60, 50, and 40 kg/cm<sup>2</sup>, respectively. Curves 5 and 4 define the termination region for a pressure drop from 30 kg/cm<sup>2</sup>.

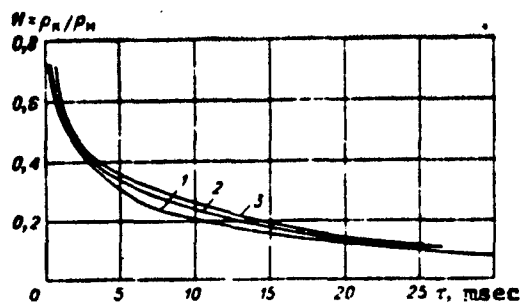


Fig. 7. Critical characteristic time of pressure drop versus reduced final pressure.  $p_m$  is 60(1), 50(2), and 40 kg/cm<sup>2</sup> (3).

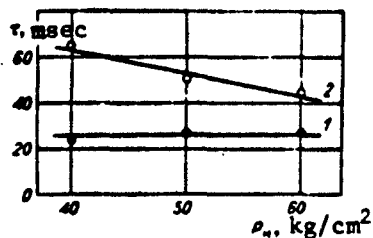


Fig. 8. Critical characteristic time (1) of pressure drop versus initial pressure for initial pressures of 40 to 60 kg/cm<sup>2</sup>, and relaxation time (2) of hot layer of foam zone, both for  $H = 0.1$ .

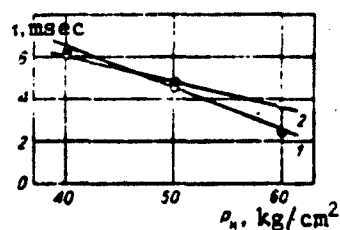


Fig. 9. Critical characteristic time (1) versus initial pressure for  $H = 0.35-0.45$ , and relaxation time (2) of hot layer versus initial pressure



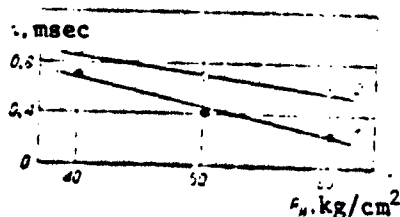


Fig. 10. Critical characteristic time (1) and relaxation time (2) of reaction layer of foam zone versus initial pressure for  $H = 0.7..$

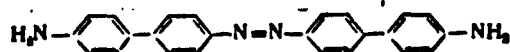
characteristic time ( $\tau_{cr}$ ) of pressure drop is the time corresponding to the  $H$  versus  $W^*$  curve, the so-called termination curve. Analysis of the data led to the following conclusion: the relaxation time of the temperature distribution in the thermal (hot) layer of the foam zone at the final pressure for the first segment of the termination curve and the relaxation time of the chemical reaction layer of the foam zone at the final pressure for the second segment of the termination curve (above the break in the curve) are the times necessary for the conversion of the initial thermal layer and initial reaction layer to the final layers, that is, to such layers as would correspond to steady-state combustion regimes. If the pressure drop has a characteristic time greater than these conversion times, the powder will burn at a nonsteady-state rate during the pressure drop; if the characteristic time is less than these conversion times, the powder combustion terminates. Thus, the experimental results only partly confirmed the conclusions of the theory (A. G. Istratov, V. B. Librovich, B. V. Novozhilov. PMTF, 1964, 3) based on Ya. B. Zel'dovich's idea that combustion termination is determined by two parameters, viz., the absolute pressure drop and the rate of drop. The fact that there are different termination curves corresponding to different initial pressures indicates the existence of a third parameter associated with the initial pressure, which was not taken into account in the theory. The parameter, evidently is associated with the fact that the temperature of the powder surface does not remain constant as Zel'dovich assumed, but can change in a nonsteady-state manner in the course of the pressure drop, and, besides, depends on the initial pressure. In addition, the course of the sloping segment of the termination curve is determined by the relaxation of the reaction layer in the foam zone.

Thermal decomposition of solid propellant. The next item [13] is by G. B. Manelis, F. I. Dubovitskiy, et al., of the Institute of Chemical Physics, AS USSR who along with A. G. Merzhanov are generally engaged [8], as was mentioned above, in work on the thermal decomposition and thermal autoignition (thermal explosion) of explosives [see for example ATD Report 67-26, Ref. 2-19 dealing with the thermal decomposition of nitro compounds]. This paper, which again was recommended for publication by Academician N. M. Emanuel', deals with the thermal decomposition of tetranitromethane (TNM) and hexanitroethane (HNE). The article notes that should the decomposition mechanism of such compounds prove to be free-radical in character, it will be feasible to determine the dissociation energy ( $D(C-N)$ ) of the C-N bond in aliphatic gem polynitro compounds of various structures from kinetic data. This circumstance prompted a study of

the decomposition mechanism and kinetics of such compounds. The decomposition of TNM and HNE was studied in the gas phase, that is, under conditions most favorable to the determination of monomolecular decomposition rates. The conditions were 86—177°C and 25—330 mm Hg partial pressures for TNM, and 90—135°C and 8—30 mm Hg for HNM. The manometric method was used under static conditions. The decomposition rate for both TNM and HNM was found to be independent of the initial vapor pressure in the above ranges. Addition of NO, NO<sub>2</sub>, I<sub>2</sub>, cyclohexene, or Ar, or a 50-fold increase of the vessel surface area did not change the decomposition rate of TNM. The decomposition is first order in the above indicated temperature ranges, with rate constants  $10^{16.3} \exp(-38300/RT)$  and  $10^{17.3} \exp(-35800/RT) \text{ sec}^{-1}$  for TNM and HNM, respectively. The data obtained in this study indicated a monomolecular mechanism of decomposition. Thermodynamic considerations led to the conclusion that the splitting off of one NO<sub>2</sub> group, e.g.,  $C(NO_2)_4 \rightarrow C(NO_2)_3 + NO_2$ , was the only possible mechanism of the first decomposition step of both TNM and HNM. The authors conclude that the free radical mechanism will probably also hold true for many other gem polynitro compounds, particularly compounds of the type, RC(NO<sub>2</sub>), RCH(NO)<sub>2</sub>, and RCX(NO<sub>2</sub>)<sub>2</sub> where X is an electronegative substituent.

The next two items dealing with thermal decomposition are coauthored by V. V. Boldyrev who, as was mentioned above, is associated [15] with the Institute of Chemical Kinetics and Combustion, Siberian Branch, AS USSR and the Scientific Research Institute of Nuclear Physics at Tomsk Polytechnic Institute and has recently been involved in work on the thermal decomposition of ammonium perchlorate (see references on p. 8). The first of these articles [14] appears to be of interest from the standpoint of the effect of additives on the thermal decomposition of propellant ingredients. It deals with the effect of certain organic semiconductor compounds, viz, polyazopolyarylenes, on the thermal decomposition kinetics of barium azide (BA) (apparently used as a model compound).

The temperature was 134°C; the amount of additive was 5%. The following compositions were investigated: 1) neat BA; 2) BA with benzidine; 3) BA with benzidine dimer,



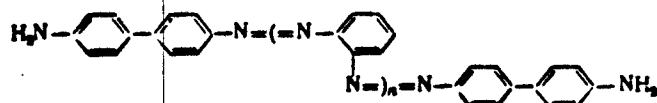
4) BA with benzidine polymer,



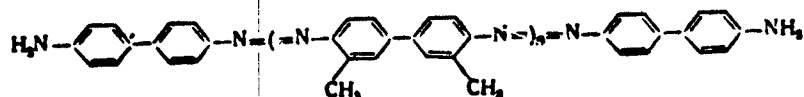
5) BA with benzidine-p-phenylenediamine copolymer,



6) BA with benzidine-o-phenylenediamine copolymer,



and 7) BA with benzidine-o-tolidine copolymer,



The results are given in the form of plots of fraction BA decomposed versus time. It was found that all the additives inhibit the decomposition of BA. The inhibiting effect of a given type of compound 1) increases with chain length; 2) increases when the chain is bent; and 3) decreases when there are substituents in the aromatic nuclei of the polymeric chain. The increase in the inhibiting effect of the additive with chain length was attributed to an increase in the electronic work function of the additive. Experiments involving metal oxide semiconductor additives confirmed that the inhibiting effect increases with the additive's electronic work function. It is postulated that the mechanism of action of the inorganic and organic semiconductor additives is similar. The determination of the relationship between the additives' chemical structure, electrical properties, and optical properties, and their inhibiting effect on BA decomposition requires a special study.

The other article by V. V. Boldyrev [15] may be pertinent from the standpoint of the effect of an external stimulus—ionizing radiation—on the thermal decomposition of certain propellant ingredients. It reports the results of an experimental study of the thermal decomposition of ammonium perchlorate with or without 5% NiO, AgN<sub>3</sub>, Ba(N<sub>3</sub>)<sub>2</sub>, Ca(N<sub>3</sub>)<sub>2</sub>, Sr(N<sub>3</sub>)<sub>2</sub> as well as of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, Ba(MnO<sub>4</sub>)<sub>2</sub>, AgMnO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, and silver oxalate. This work was done because irradiation during thermal decomposition was expected 1) to have an effect qualitatively different from prior irradiation, and 2) to make it possible to determine the role of the step of electron excitation to the conduction band, a step in the decomposition scheme of many salts which in a number of cases is considered to be rate-controlling. It was found that irradiation during thermal decomposition accelerates the decomposition in the case of KMnO<sub>4</sub>, Ba(MnO<sub>4</sub>)<sub>2</sub>, AgMnO<sub>4</sub>, silver oxalate, Ba(N<sub>3</sub>)<sub>2</sub>, Ca(N<sub>3</sub>)<sub>2</sub>, Sr(N<sub>3</sub>)<sub>2</sub>, and NH<sub>4</sub>ClO<sub>4</sub> containing 5% NiO, but has no effect on the decomposition rate of Ag<sub>2</sub>O, AgN<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, NH<sub>4</sub>Cr<sub>2</sub>O<sub>7</sub>, and neat NH<sub>4</sub>ClO<sub>4</sub>. A

mechanism of action of the irradiation, similar to the mechanism of action of prior irradiation, was postulated. This mechanism involves activation of the solid phase by the irradiation, as for example, as a result of the formation of radiolysis products which catalyze the decomposition. The fact that irradiation during thermal decomposition has no specific effect as compared with prior irradiation indicates that the electron excitation step is not rate-controlling in the thermal decomposition of the compounds studied.

**Ignition.** An article [16] is coauthored by S. M. Kogarko, who has recently been engaged in work dealing with the combustion mechanism and combustion stability of gaseous fuels (ATD Reports 66-146, Entry 5; 67-26, Ref. 2-34; 67-32, Ref. 3-8, 68-32-107-2, Ref. 34] and A. A. Borisov, who with S. M. Kogarko was recently involved in research on the thermal decomposition of nitromethane [ATD Report 66-146, Entry 8]. This item reports the results of an experimental study of the ignition and combustion behind a reflected shock wave, of particles stirred up from a layer of finely divided fuel by a passing shock wave. The article notes that the results may be of interest for the study of the kinetics of heterogeneous combustion reactions. This suggests that such systems may represent models for the study of composite or hybrid combustion. The experiments were carried out in a shock tube 22 mm internal diameter and 4.5 m long; the high-pressure section containing nitrogen or helium was 1.15 m long. The low pressure section was filled with air; near the end was placed a thin layer ( $h = 0.1-0.2$  mm) of the powdered solid fuel. The fuel used was charcoal, brush carbon, or black powder. In most experiments the particle size was less than  $50 \mu$ ; in some of the experiments with brush carbon, to determine the effect of particle size on ignition, the particle size was varied from 140 to  $320 \mu$ . Some experimental results are given in Fig. 11. The data indicate that the fuels ignite behind shock waves at  $M = 2.25$  and above with different ignition delays. The minimum ignition temperature was about  $900^\circ K$  for the

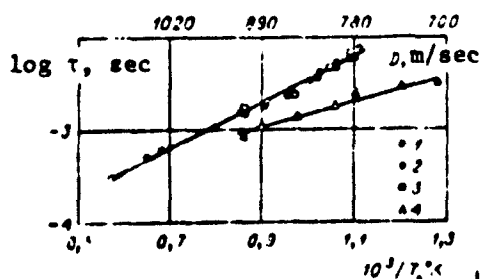


Fig. 11. Ignition delay versus reciprocal temperature behind reflected shock wave in air ( $p_0 = 0.1-0.5$  atm) and versus shock wave velocity

1 - Charcoal ( $\leq 50 \mu$ ); 2 - brush carbon ( $\leq 50 \mu$ ); 3 - brush carbon (140-320  $\mu$ ); 4 - black powder ( $\leq 50 \mu$ ).

carbons and  $800^\circ K$  for black powder. Pressure oscillographs showed that pressure behind the reflected shock front at the end of the tube remains constant for about 1.5 msec, then increases for 6-8 msec. Ignition behind weak shock waves ( $M < 2.6$ )

takes place with a delay of 2—6 msec so that the temperatures given in Figure 1 for ignition delays of more than 1.5 msec are somewhat low since such temperatures were calculated from falling shock wave velocities. The ignition temperature was independent of particle size within the limits of the experimental deviation. The following ignition mechanism was postulated: after the shock wave reaches the end of the tube, the fuel is lifted into the air on account of hydrodynamic instability. Then, the particles suspended in the air ignite in the reflected shock wave after a certain delay, and are completely consumed provided there is enough oxidizer.

Thermal explosion. Two articles coauthored by A. G. Merzhanov of the Institute of Chemical Physics, AS USSR deal with the area of thermal explosion. As mentioned above, A. G. Merzhanov has been previously identified with experimental and theoretical work in the field of thermal autoignition (thermal explosion) of explosives [ATD Reports 57-32, Ref. 3-1, 3-14; 67-33, 4-1; 68-29-106-1, Ref. 11, 12; 68-30-106-2, Ref. 21; this Report, Ref 8]. In the first item [17], a theoretical article, recommended for publication by the prominent Academician N. N. Semenov, dimensionless formulas for the induction period  $\tau_{ind}$  of a thermal explosion in a hypothetical solid are derived for all values of dimensionless temperature  $\theta_0 \geq 0$  and for boundary  $\theta_0$  values. The formula

$$\tau_{ind} = 1 + \sum_{m=1}^{\infty} x^m \sum_{k=1}^m \frac{A_m^k}{(m+1)^{k+1}} \theta_0^{m-k}, \quad (3)$$

where  $x = Qk_0EV \exp(-E/RT_*) / \alpha SR_*^2$ ,  $\theta_0 = (T_* - T_0)E/RT_*^2$ , and  $A_m^k$  is the number of permutations of  $m$  terms taken  $k$  at a time, is derived for  $\theta_0 \geq 0$  by integration of the fundamental heat balance equation in dimensionless form and series expansion of the subintegral function. In the above expressions,  $Qk_0$  is the product of the heat of reaction and preexponential factor,  $E$  is the activation energy,  $S/V$  is the ratio of the heat exchange surface area to the volume of the reacting system,  $R$  is the gas constant,  $\alpha$  is the heat transfer coefficient,  $T_*$  and  $T_0$  are the characteristic and ambient temperatures, respectively. In the present case, the initial temperature of the substance ( $T_1$ ) is taken

as  $T_*$ . ( $T_1 \geq T_0$ ). In the case of an adiabatic thermal explosion, when  $\kappa \rightarrow \infty$ ,  $\tau_{ind} = 1$ , in agreement with literature data. Formula (3) becomes

$$\tau_{ind} = 1 + \sum_{m=1}^{\infty} \frac{m!}{(m+1)^{m+1}} \left(\frac{\theta}{\Delta}\right)^m, \quad (4)$$

or

$$\tau_{ind} = \text{Alog} \frac{\Delta}{\Delta-1}, \quad (5)$$

where  $\Delta = \kappa/\kappa_{cr}$  is the distance from the boundary of the thermal explosion, for low or high  $\theta_0$ , respectively. The case of low  $\theta_0$  is the classical case,  $T_1 = T_0$ . Thermal explosion in an adiabatically compressed gas is an example of high initial overheating (high  $\theta_0$ ). A plot of  $\tau_{ind}(\Delta)$  for two boundary cases shows a weak dependence of  $\tau_{ind}$  on  $\theta_0$  at  $\Delta = \text{const}$ . Introduction of a correction factor,  $\beta = RT_*/E$ , into the fundamental heat equation gives

$$\tau_{ind}(\beta) \approx \tau_{ind}(\theta) [1 + \epsilon \beta], \quad (6)$$

where

$$\epsilon = \frac{1}{\tau_{ind}^{(1)}} \sum_{m=1}^{\infty} m^{-2} \kappa^{1-m} \sum_{k=0}^{m-1} \frac{m! (m+1-k)! \theta_0^k}{k! m^{m-k}},$$

$\epsilon$  is shown to increase at increasing  $\Delta$  and with decreasing  $\theta_0$ .  $\epsilon$  was maximum ( $\epsilon=2$ ) under adiabatic conditions ( $\Delta \rightarrow \infty$ ).

The other item [18] reports the development of a new, more general and effective experimental dynamic method than heretofore available for determining the critical static temperature ( $T_*$ ) of thermal explosion for a self-accelerating reaction in a condensed substance. It is noted that experimental determination of the critical conditions of such explosions by conventional static methods is difficult due to the length of the induction period; dynamic methods based on initial heating of the substance above  $T_*$  with subsequent cooling, shorten the induction period and, hence, save time. A method previously proposed by the authors involved linear measurement of the tem-

perature ( $T_0$ ) of the surrounding heat transfer agent (linear heating and linear cooling). In contrast, the new method is based on regulation of  $T_0$  according to

Table 1. Comparison of  $T_*$  determined by dynamic and static methods (no temperature gradient in reaction zone)

Substance	d, cm	l, d	$\rho$ , g/cm <sup>3</sup>	$T_{init}$ , °C	$b = \text{const}$	$T_{0 \text{ min}}$ , °C	$T_{\text{dyn}}$ , °C	$T_{\text{stat}}$ , °C
tetryl	0,45	$\frac{1}{5}$	1,5	153	4,5	$\frac{146,5}{139,5}$	$\frac{140,0}{142,0}$	$\frac{150,5}{142,5}$
pyroxylin	0,54	2	1,4	170	$\frac{2,5}{3,3}$ 4	$\frac{150}{152}$ 153	$\frac{156,5}{156,5}$ 156,0	155,5
ammonium bichromate	0,8	2	2	218	3,0	209,5	212,5	212,5
silver oxalate	0,76	1,7	3,5	$\frac{163}{162}$	$\frac{1,5}{3}$	$\frac{155}{157}$	$\frac{157,5}{157,5}$	156

Table 2. Comparison of  $T_*$  determined by dynamic and static methods (temperature gradient in reaction zone)

Substance	$\phi$	d, cm	l, d	$\rho$ , g/cm <sup>3</sup>	$T_{\text{init}}$ , °C	$b = \text{const}$	$T_{0 \text{ min}}$ , °C	$T_{\text{dyn}}$ , °C	$T_{\text{stat}}$ , °C
pyroxylin	5,5	4	1	1,5	99	6	92	96,5	95
Substance No 2	5,5	$\frac{2}{4}$ 5	2	1,6	$\frac{186}{181}$ 170 175	$\frac{2,8}{5,1}$ 3,5 2,8	$\frac{161,5}{165}$ 142 136	$\frac{173}{171,0}$ 151,0 147,5	171 153 147,0
Ammonium bichromate	20	1,2	1,6	2	221	4	216,5	221,0	219,0

the servo principle.  $T_0$  is changed in such a way that the temperature difference (b) between the center of the sample and the heat transfer agent remains constant at a predetermined level during the process,  $b = T - T_0 = \text{const}$ , that is, the rate

of heat removal from the reaction zone remains constant. A formula was derived for calculating  $T_*$  in the case where there is no temperature gradient in the reaction zone:

$$T_* = T_{0\min} + b_* [b b_* - \ln(b b_*) - 1]. \quad (7)$$

where  $b_*$ , the maximum preexplosion temperature difference can be calculated from the formula:

$$b_* = \frac{(T_{0\min} - T_{0\min}) + (b'' - b')}{\ln(b'' b')}, \quad (8)$$

To determine  $T_*$ , two experiments (' and ") with different predetermined  $b$  and  $b_*$  are required to obtain two values of  $T_{0\min}$ . In the case where there is a temperature gradient in the reaction zone, Equation (7) is also suitable for calculating  $T_*$ , provided  $b = \bar{b} = \bar{T} - T_0$ , where  $\bar{T}$  is the volume-average reaction zone temperature;  $\bar{b}$  for a cylindrical sample can be calculated from

$$\bar{b} = b_u + 2b_* [1 - (a^2 + 1) \ln(a^2 + 1) a^2], \quad (9)$$

where  $b_u$  is the  $b$  for a cylindrical sample,

$$b_u = 2b_* \ln(a^2 + 1) + \frac{4b_* a^2}{\pi(a^2 + 1)}. \quad (10)$$

The experiment was conducted at different values of the Bi criterion. The initial  $T_0$  was selected so that the time for the establishment of a constant  $b$  in the system be as short as possible. The substances used were tetryl, pyroxylin, ammonium bichromate, silver oxalate, and substance No. 2 [unspecified]. All except tetryl were in the form of pressed pellets with different densities and height/diameter ratios. Analysis of the experimental results (some of which are given in Tables 1 and 2) indicates that the proposed method enables the determination of the critical static temperature with accuracy and a saving of time over conventional static methods.



**Detonation.** The first three items in this section concern detonation of *nitroorganics and nitrate esters which are generally of interest as monopropellants, oxidizers, and plastizer additives.* A. N. Dremine, who has previously [ATD Reports 67-33, Ref. 4-9; 68-30-106-2, Ref. 19 and 20] been involved in work on the detonation of *nitroorganics and nitrate esters*, is the coauthor of an article [19] dealing with an experimental study of the initiation and propagation of the reaction caused in liquid explosives by an irregularity of the incident shock wave surface. This work was done in view of the difficulty in obtaining accurate quantitative data on the pressure dependence of the induction period  $\tau$  and on the phenomena associated with the structure of the detonation front. The experiments were conducted with 75/25 and 60/40 nitromethane-acetone mixtures. Irregularities of the shock front were created either by placing a metal strip on the bottom of the container with the liquid explosive or by cutting a groove in the bottom and filling it with a TNT-RDX cast alloy. A TNT tablet served as booster charge. Perturbations at the shock front were detected by observing and photo-recording scattered light from an argon lamp. Pressures of the incident shock were in the 60000—100000 atm range. During the induction period the liquid explosive behaved as an inert substance. The observed triple configurations at the shock front (Fig. 12) consisted of the main direct shock wave, an oblique lateral wave,

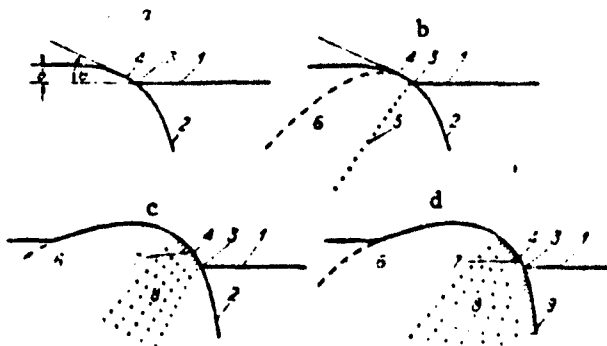


Fig. 12. Possible types of triple configurations generated by propagating transverse-perturbations

1 - Main incident shock wave; 2 - transverse wave; 3 - shock front curvature; 4 - oblique shock wave; 5 - trajectory of reaction discontinuity; 6 - region of effects due to perturbations from reactions; 7 - oblique wave with reaction; 8 - reaction products; 9 - transverse reaction wave.

and a transverse wave. All four types of configurations (12a, 12b, 12c, and 12d) were observed at pressures in the 75000—100000 atm range in both explosive mixtures studied. The occurrence of a particular configuration depended on the distance  $\delta$  between the plane shock wave initiated at the strip and the main shock wave initiated at the bottom plate. This distance, a measure of the shock front perturbation, was determined by the expression,  $\delta = h (1 - D_1/D_2)$ , where  $h$  is the height of the strip, and  $D_1$  and  $D_2$  are velocities of the shock wave in the liquid studied and in the bottom barrier, respectively. Photorecordings of the process

showed trajectories of the reaction discontinuity at  $\delta < 0.5$  mm (Fig. 12b). Sometimes an additional glow may be formed above the trajectory at  $\delta = 0.5$  mm. Expansion of the reaction zone was observed at  $\delta > 0.5$  mm. The angle ( $\theta$ ) formed by the reaction front and the main shock wave was small ( $5-7^\circ$ ) in the experiments with thin liquid layers at  $\delta = 0.5$  mm (Fig. 12c) and the glow was very bright because of the ejection of reaction products. At  $\delta > 1.2$  mm, a foreglow was observed due to an additional transverse reaction wave (Fig. 12d). A new reaction configuration propagating in the opposite direction was formed at  $\delta = 1$  mm with an induction period  $\tau_1 = 2.5$   $\mu$ sec. A new type of consecutively propagating irregularity was detected in the process initiated by the transverse perturbation in the 60/40 explosive mixture. New configurations were generated by thermal explosion in the shock-compressed explosive. Different modes of interactions between two reaction discontinuities favored reaction propagation in the 75/25 mixture and termination in the 60/40 mixture. All the types of artificial configurations observed in the study are believed to also occur at a normal detonation front.

N. M. Kuznetsov and K. K. Shvedov, the authors of a previously published article dealing with the equation of state of detonation products of RDX [ATD Report 87-33, Ref. 4-25] have written a paper [20] concerned with the isentropic expansion of these detonation products. The total pressure ( $p$ ), thermal component of pressure ( $p_t$ ), work of adiabatic expansion of the detonation products of hexogen ( $R = -sp \, dp/\rho^2$ ), velocity of sound ( $c$ ), and isentropic exponent ( $n$ ) were calculated as a function of density ( $\rho$ ) for the cases of isentropic expansion from Jouguet points or from initial states. The calculations were made by numerical integration of the equation  $dE = p \, dp/\rho^2$  (11), where  $E$  is the internal energy, and of the equation of state of the detonation products, which was derived earlier by the authors [Ibid]. Equation (11) expresses the condition of constant entropy, which is necessary for the study of the gas dynamics and kinetics of scattering of detonation products. Evaluation of the tabulated data showed the same pattern of change of  $p/\rho$  with  $\rho$  in both cases of isentropic expansion.  $p_t$  increased rapidly in relation to  $p$  on expansion from the maximum  $\rho$  (2.4 g/cc) and the  $p_t/p$  ratio reached the value of 1 at  $\rho = 0.8$  g/cc. The same relationship between the elastic and the thermal components of pressure is postulated to exist for all explosives with high calorific value. The value of  $n$  at high initial  $\rho$  (down to 0.8 g/cc) fluctuated within the 2.7-3 range and exhibited a broad peak on isentropic expansion from the high density states ( $\rho = 2.4-1.4$ ). The existence but not the position of the  $n$  maximum was in agreement with earlier literature data [V. N. Zubarev, PMTF, 1965, 2]. The calculated  $c$  values were found to be in agreement within 20% with the earlier experimental data of the authors over the entire range of  $\rho$  (0.7-2.4 g/cc) in the Jouguet points. The change in  $n$  and  $c$  on expansion from the initial states (instantaneous explosion) is shown in Fig. 13. The ratios  $p/p'$  and  $T/T'$  of pressure and temperature in the Jouguet point and in the

products of instantaneous explosion are plotted in Fig. 14 versus initial charge density  $\rho_1$ . This behavior of  $p/p'$  and  $T/T'$  with  $\rho_1$  must be taken into account on

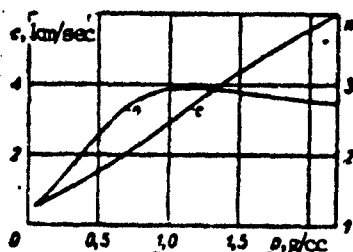


Fig. 13

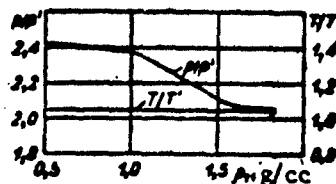


Fig. 14

substitution of the parameters of instantaneous explosion for the parameters of real detonation. The calculated value of the work of adiabatic expansion to  $p = 0$  ( $R_\infty$ ) in the case of instantaneous explosion was found to be in good agreement with the experimental values of the heat of explosion  $Q$ . The ratios of  $R$  experimental to  $R$  calculated for instantaneous explosion were found to be nearly equal to the earlier determined maximum work efficiencies on expansion to atmospheric pressure.

An experimental study on the example of TNT of the effect of charge size on the so-called chemical losses which are due to the scattering of unreacted or partly reacted material from the reaction zone during detonation is the subject of a paper [21]. The paper notes that losses of a certain magnitude decrease the detonation velocity by lowering the pressure in the reaction zone and the shock front, while losses of another magnitude decrease the mechanical effect of the explosion. In this particular case, the effect of charge size on losses decreasing the mechanical effect of the explosion is considered on the basis of experimental data on the impulse of explosion products. The impulse was determined for explosions of loose-packed, cast, and pressed cylindrical TNT charges of different particle sizes. It was found that for TNT, and probably for other homogeneous explosives as well, the equivalent thickness of the layer of losses decreases with increasing radius and tends toward some constant value, probably substantially lower than the critical radius. At low charge diameters (in the vicinity of the critical diameter), for homogeneous explosives, losses increase with increasing particle size of the charge, and, in general, with increasing critical radius. With increasing charge diameter, the difference in the magnitude of losses for charges of different particle sizes decreases.

The last item [22] in this section reports the results of an experimental study of the principal factors which determine the effect of the properties of the casing of the charge on detonation velocity. It is noted that the effect of the properties of the casing on the possibility and propagation velocity of detonation becomes apparent when the charge diameter is less than the limiting diameter. Ammonium perchlorate-RDX charges (39/61) either loose-packed or pressed, 10 and 20 mm in diameter, 1.1 and 1.76 g/cm<sup>3</sup> in density, respectively, were used. The case material was plexiglass, iron, copper, or lead; the casing thickness was 1, 3, 5, 6 and 7.5 mm. It was found that the effect of the case material on the detonation velocity decreases in the order, iron, copper, lead, plexiglass (see Table 3). For a given material, the detonation velocity was highly dependent on casing thickness. The case hinders the radial expansion of detonation products. The angle of expansion of the case was calculated for all

Table 3. Detonation velocity of a 39/61 ammonium perchlorate-RDX mixture

Plexiglass case		Lead case		Copper case		Iron case	
Thickness, mm	D, m/sec	thickness, mm	D, m/sec	thickness, mm	D, m/sec	thickness, mm	D, m/sec
Loose packed charge ( $\rho = 1.1 \text{ g/cm}^2$ )							
1	-	1	-	1	5520	1	5680
3	5390	3	5530	3	5660	3	5850
5	5380	5	5640	5	5850	5	6000
				7	5860	7,5	6020
Pressed charge ( $\rho = 1.76 \text{ g/cm}^2$ )							
1	7820	1	-	1	7900	1	8400
3	7860	-	-	3	8050	3	8480
5	7830	5	8080	5	8220	5	8590

the materials; with the exception of plexiglass, the difference between angles of expansion of the different materials was small and, hence, fails to explain the experimentally observed effect of the case material on detonation velocity. The dynamic compressibility of the case material did have a substantial effect on detonation velocity; the lesser the compressibility, the greater the detonation velocity, other things being equal. The tensile strength of the material also had an effect; at a given compressibility, detonation velocity increased with the tensile strength of the case. No substantial effect of case mass on detonation velocity was revealed in the experiments.

# REFERENCES

1. Yeremenko, L. T.; Natsibullin, F. Ya.; Nesterenko, G. N. Radical synthesis of 1,1,1,6,6,6-hexanitrohexane. AN SSSR. Izvestiya. Seriya khimicheskaya, no. 12, 1967, 2780.
2. Kolesnikov, G. I.; Buksh, Ye. L.; Rud', V. A. Propellant for model rockets. Class 78, No. 205662. Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki, no. 23, 1967. 201-202.
3. Malakhov, V. I.; Palitsyn, N. P.; Piskunova, Ye. M. Production of ferrocene on a pilot plant scale. Zhurnal prikladnoy khimii, v. 40, no. 11, 1967, 2574-2576.
4. Balashov, D. E. Thermodynamic properties of nitroglycerin powders at pressures up to 26,000 kg/cm<sup>2</sup> and temperatures of 20-92°C. V. Study of isentropic processes. Zhurnal fizicheskoy khimii, v. 41, no. 11, 1967, 2793-2798.
5. Belyakov, G. V.; Vilenskaya, G. G. Equation of state of trinitrotoluene. AN SSSR. Doklady, v. 177, no. 5, 1967, 1050-1053.
6. Pereverzev, A. Ye.; Vlasov, D. A.; Chernykh, V. D. X-ray and electron microscope study of the phase boundary NH<sub>4</sub>ClO<sub>4</sub>-ED-5 [epoxy resin]. Zhurnal prikladnoy khimii, v. 40, no. 11, 1967, 2405-2513.
7. Nevostruyev, V. A.; Bugayenko, L. T.; Zakharov, Yu. A. Radiolysis of ammonium perchlorate. Khimiya vysokikh energiy, no. 4, 1967, 406-407.
8. Belyayev, A. F.; Bakhman, N. N. Review of K. K. Andreyev's book Thermal Decomposition and Combustion of Explosives. Fizika goreniya i vzryva, v. 3, no. 2, 1967, 318-319.
9. Kaganov, S. A. Theory of combustion of gases and condensed substances. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 5, 1967, 111-115.
10. Glazkova, A. P.; Popova, P. P. Combustion inhibitors of ammonium nitrate and ammonium perchlorate and their mixtures [with fuels]. AN SSSR. Doklady, v. 177, no. 6, 1967, 1341-1344.
11. Ivanov, G. V.; Shibayev, G. I.; Komarov, V. F.; Boldyrev, V. V. Combustion of ammonium perchlorate mixtures with various organic substances. Fizika goreniya i vzryva, v. 3, no. 2, 1967, 315-317.

12. Marshakov, V. N.; Leypunskiy, O. I. Powder combustion and its termination during a rapid pressure drop. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 231-235.
13. Nazin, G. M.; Manelis, G. B.; Dubovitskiy, F. I. Thermal decomposition of tetranitromethane and hexanitroethane in the gas phase. AN SSSR. *Doklady*, v. 177, no. 5, 1967, 1128-1130.
14. Komarov, V. F.; Skorik, A. I.; Boldyrev, V. V.; Terpugova, M. P.; Kotlyarevskiy, I. L. Effect of organic semiconductor additives on the thermal decomposition of barium azide. *Vsesoyuznoye khimicheskoye obshchestvo. Zhurnal*, v. 12, no. 6, 1967, 695-696.
15. Skorik, A. I.; Boldyrev, V. V.; Komarov, V. F. Thermal decomposition of ionic salts during x-ray irradiation. *Kinetika i kataliz*, v. 8, no. 6, 1967, 1258-1264.
16. Borisov, A. A.; Kozenko, V. P.; Lyubimov, A. V.; Kogarko, S. M. Ignition of powdered fuels behind shock waves. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 308-309.
17. Merzhanov, A. G.; Yu. M. Grigor'yev. Analytical solution of the simplest nonstationary problem of a nonadiabatic thermal explosion. AN SSSR. *Doklady*, v. 176, no. 6, 1967, 1344-1346.
18. Merzhanov, A. G.; Strunina, A. G.; Abramov, V. G. Dynamic regimes of thermal explosion. V. Method for experimental determination of critical conditions of thermal explosion of self-accelerating reactions with a shortened induction period. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 242-247.
19. Buravova, S. N.; Drem'in, A. N.; Yakushev, V. V. Propagation of and interactions in triple shock wave configurations in liquid explosives. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 188-196.
20. Kuznetsov, N. M.; Shvedov, K. K. Isentropic expansion of detonation products of hexogen. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 203-210.
21. Rempel', G. G. Effect of charge size on the magnitude of chemical losses [during detonation]. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 211-216.
22. Akimova, L. N.; Apin, A. Ya. Effect of shell material and thickness on the detonation velocity of an ammonium perchlorate-RDX mixture. *Fizika gorennya i vzryva*, v. 3, no. 2, 1967, 197-202.